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(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Amino-Functional Polyester Resins

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5,089,1/44

Notice: This application is as filed and may therefore contain an incomplete specification.



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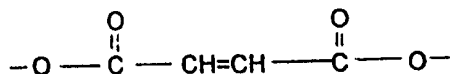
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AMINO-FUNCTIONAL POLYESTER RESINSABSTRACT OF THE DISCLOSURE

The present invention relates to a process for the production of polyester resins containing 0 to 10% by weight of hydroxyl groups and 0.01 to 9%, preferably 0.05 to 2%, by weight of nitrogen (expressed as N = 14) in the form of primary and/or secondary amino groups, by reacting in an addition reaction at 0 to 120°C

- i) polyester resins having a molecular weight (M_n) of 286 to 10,000 and containing an average per molecule of at least 2 structural units corresponding to the formula:



and optionally alcoholic hydroxyl groups with

- ii) ammonia or primary monoamines corresponding to the formula:



wherein

R represents an aliphatic, cycloaliphatic or araliphatic radical optionally containing ether oxygen atoms and/or hydroxyl groups.

The present invention also relates to the amino-functional and optionally hydroxy-functional polyester resins obtained by this process and to their use as a binder component in two-component polyurethane coating compositions, particularly for coating plastic moldings.

AMINO-FUNCTIONAL POLYESTER RESINSBACKGROUND OF THE INVENTIONField of the Invention

- 5 The present invention relates to a new process for the production of amino-functional and optionally hydroxy-functional polyester resins, to the resins obtained by this process and to their use as a binder component in two-component polyurethane coating compositions.

Description of the Prior Art

- 10 Two-component polyurethane coating compositions are known and are suitable for the production of high-quality coatings which can be made hard, elastic, abrasion resistant, solvent resistant and, above all, weather resistant. The basic chemistry of these lacquers and coatings is described inter alia in "Lackkunstharze", Hans-Wagner/Hans Friedrich
15 Sarx, Carl Hanser Verlag, München, pages 153 to 173 (1971). The polyesters described as resin component almost exclusively contain hydroxyl groups which react with the polyisocyanates used as curing agents to form polyurethanes.

- 20 The reaction between the OH and NCO groups proceeds so slowly at room temperature that economical, i.e., rapid, drying is only possible at elevated temperatures. Although the relatively slow reaction at room temperature can be accelerated by catalysts, the resulting coatings are adversely affected, for example, in their hardness, by the catalysts used (S. Günther, Ind. Lackierbetr. 57 (1989), No. 5, page 167).

- 25 The possibility of using the very much faster reaction between aliphatic amines and isocyanates has not satisfactorily been used in practice due to the extremely high reaction rate which prevents a controlled reaction. The fairly sluggishly reacting aromatic amines cannot be used for top coats due to their pronounced tendency towards
30 yellowing.

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EP-A-0,403,921 describes a simple process for reducing the excessive reactivity of aliphatic amines. This process is based on the addition of primary amines onto maleic acid esters which gives secondary amino groups that react with isocyanate groups in the coating system. The main concern of this process was the presence of low molecular weight, low-viscosity aminic chain-extending agents for two-component polyurethane coating compositions.

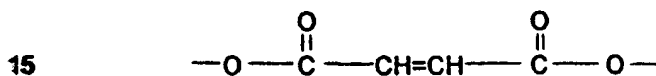
It has now been found that relatively high molecular weight polyester resins, which, in addition to the optional presence of alcoholic hydroxyl groups, are distinguished by a readily adjustable and controllable content of primary or secondary amino groups incorporated in the α -position to the ester groups, are particularly valuable binder components for two-component polyurethane coating compositions. These amino-functional polyester resins are produced by addition of ammonia or primary monoamines onto polyester resins containing olefinically unsaturated structural units of the type described in more detail hereinafter to form primary or secondary amino groups.

Although the production of amino-functional polyester resins by addition of amine onto unsaturated polyester polyols is already known from EP-A-0,273,243, the amines mentioned there as starting material are diamines containing two primary amino groups. The products of this reference are distinguishable from the products of the present invention, which are described in detail hereinafter, in particular by the presence of primary amino groups which are not arranged in the α -position to the ester groups (referred to in the Examples as "basic nitrogen") and which therefore show a reactivity to isocyanate groups which is much higher than that of the amino groups present in the end products according to the invention. In addition, the end products of the reference are not

recommended as a binder component for two-component polyurethane coating compositions, but instead for the production of adhesives and foams.

SUMMARY OF THE INVENTION

5. The present invention relates to a process for the production of polyester resins containing 0 to 10% by weight of hydroxyl groups and 0.01 to 9%, preferably 0.05 to 2%, by weight of nitrogen (expressed as N = 14) in the form of primary and/or secondary amino groups, characterized by reacting in an addition reaction at 0 to 120°C
- 10 i) polyester resins having a molecular weight (M_n of 286 to 10,000 and containing an average per molecule of at least 2 structural units corresponding to the formula:



and optionally alcoholic hydroxyl groups with

- ii) ammonia or primary monoamines corresponding to the formula:



wherein

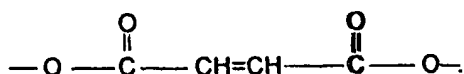
R represents an aliphatic, cycloaliphatic or araliphatic radical optionally containing ether oxygen atoms and/or hydroxyl groups.

The present invention also relates to the amino-functional and

- 25 optionally hydroxy-functional polyester resins obtained by this process and to their use as a binder component in two-component polyurethane coating compositions, particularly for coating plastic moldings.

DETAILED DESCRIPTION OF THE INVENTION

The olefinically unsaturated polyester resins used in the process according to the invention generally have an acid value below 10, preferably below 3 mg KOH/g; a hydroxyl value of 0 to 325, preferably 0 to 250 mg KOH/g, which corresponds to a hydroxyl group content of 0 to 10%, preferably 0 to 7% by weight; a molecular weight (M_n , which may be calculated from the stoichiometry of the starting materials) of 286 to 10,000, preferably 488 to 8,000; and an average of at least 2, preferably at least 3, structural units corresponding to the formula:



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In a preferred embodiment, the unsaturated polyester resins are produced by esterifying

- a) a polycarboxylic acid component containing maleic acid, maleic anhydride and/or fumaric acid, and optionally up to 95 carboxyl equivalent-%, based on the total equivalents of component (a), of other polycarboxylic acids having a molecular weight of 118 to 1,000, preferably of 118 to 400 and/or anhydrides of such acids with
- b) a polyol component having an maximum average hydroxyl functionality of 3 and containing at least one polyhydric alcohol having a molecular weight of 62 to 400 and
- c) optionally a monocarboxylic acid component in a quantity of up to 50 carboxyl equivalent-%, based on the total equivalents of components a) and c), and containing at least one monocarboxylic acid having a molecular weight of 60 to 400 and/or at least one

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anhydride of such monocarboxylic acids and

- d) optionally a monohydric alcohol component in a quantity of up to 50 hydroxyl equivalent-%, based on the total equivalents of components b) and d), and containing at least one monohydric alcohol having a molecular weight of 32 to 400,

while maintaining an equivalent ratio of carboxyl groups to hydroxyl groups of 1:1.5 to 1:1 and terminating the reaction when the acid value is below 10 mg KOH/g.

- Suitable polycarboxylic acids or polycarboxylic anhydrides a) other than those mentioned include succinic acid, glutaric acid, adipic acid, isophthalic acid, phthalic acid, terephthalic acid, phthalic anhydride, tetrahydrophthalic acid, tetrahydrophthalic anhydride, hexahydrophthalic acid, hexahydrophthalic anhydride, trimesic acid, trimellitic acid, commercial dimer or trimer fatty acids and trimellitic anhydride. Adipic acid is particularly preferred as the other acid a).

- Suitable polyhydric alcohols b) include ethylene glycol, 1,2- and 1,3-propanediol, 1,2- and 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol (2,2-dimethyl-1,3-propanediol), 1,4-bis-(hydroxymethyl)-cyclohexane, cyclohexane-1,2- and -1,4-diol, 2,2-bis-(4-hydroxycyclohexyl)-propane, octahydro-4,7-methano-1H-indene dimethanol, trimethylol propane, glycerol and/or pentaerythritol.

- Optional monocarboxylic acids or monocarboxylic anhydrides c) include acetic acid, propionic acid, n-octanoic acid, 2-ethylhexanoic acid, stearic acid, benzoic acid, anhydrides of these acids and mixtures of monocarboxylic acids and/or monocarboxylic anhydrides. Olefinically unsaturated monocarboxylic acids (such as acrylic acid or methacrylic acid) and unsaturated fatty acids or mixtures thereof (such as soybean fatty acid or dehydrated castor oil fatty acid) may also be used

as, or as part of, component c) in the process according to the invention. Hydroxy-functional carboxylic acids (such as hydrogenated castor oil fatty acid, hydroxybenzoic acid and/or lactones, in particular ϵ -caprolactone) may also be used.

- 5 Optional alcohol component c) is selected from monohydric alcohols such as methanol, ethanol, the isomeric propanols, butanols and hexanols, cyclohexanol, benzyl alcohol, fatty alcohols and mixtures of these alcohols.

- The unsaturated polyesters are produced from the starting materials mentioned by way of example by known methods as described, for example, in "Ullmanns Encyclopädie der technischen Chemie", Verlag Chemie, Weinheim, 4th Edition (1980), Vol. 19, pages 61 et seq.; by H. Wagner and H.F. Sarx in "Lackkunstharze", Carl Hanser Verlag, München (1971), pages 85 et seq.; by G. Gerber and H. Gruber in "Houben-Weyl", Methoden der organischen Chemie, Vol. E 20, Part 2, pages 1405 et seq.; or by R. Dhein, D. Reuter and G. Ruf, ditto, pages 1429 et seq. The esterification is optionally carried out in the presence of a catalytic quantity of a typical transesterification catalyst, e.g., acids, bases or transition metal compounds, such as titanium tetrabutylate, at 15 approx. 80 to 260°C, preferably 100 to 230°C. The esterification reaction is continued until the required hydroxyl and acid values are reached. 20 The type and quantities of components a) to d) used are selected so that the polyesters have the characteristics described above.

- The equivalent ratio of carboxyl groups to hydroxyl groups is 25 generally 1:1.5 to 1:1, preferably 1:1.3 to 1:1. Anhydride groups correspond to 2 carboxyl groups and are included as such in the calculation.

The production of the unsaturated polyester resins may also be

carried out by transesterifying esters based on polycarboxylic acids and monohydric, readily volatile alcohols in combination with polyhydroxyl compounds example or by using esters based on monohydric, readily volatile carboxylic acids and polyhydroxyl compounds in combination with
5 polycarboxylic acids with elimination of the readily volatile alcohol or the readily volatile acid. However, this method of producing the polyester resins is less preferred.

In the process according to the invention, the olefinically unsaturated polyester resins are reacted with ammonia or primary
10 amines corresponding to the formula:



wherein

R represents an aliphatic, cycloaliphatic or araliphatic radical which may contain ether groups and/or hydroxyl groups, preferably an
15 aliphatic or cycloaliphatic hydrocarbon radical having up to 15 carbon atoms and optionally at least one alcoholic hydroxyl group.

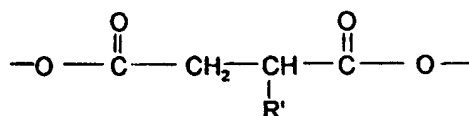
Primary monoamines corresponding to the above formula wherein the primary amino group is attached to a secondary or tertiary carbon atom, are particularly preferred reactants for the unsaturated polyester
20 resins.

Suitable amines corresponding to the above formula include methyl amine, ethyl amine, 1-aminopropane, 2-aminopropane, 1-aminobutane, 2-aminobutane, 1-amino-2-methyl propane, 2-amino-2-methyl propane, 2-amino-2-methyl butane, 1-aminohexane, 1-amino-2-ethyl hexane, 1-aminodecane, 1-aminododecane, 1-aminotetradecane, 1-aminohexadecane, 1-aminooctadecane, allyl amine, cyclohexyl amine, 2-,
25 3- or 4-methyl cyclohexyl amine, aminomethyl cyclohexane, 3,3,5-trimethyl cyclohexyl amine, 1-aminomethyl-3- or 4-methyl-3-cyclohexene,

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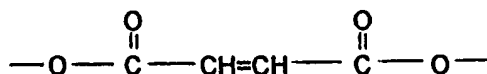
benzyl amine, cyclopentyl amine, cyclooctyl amine, cyclopropyl amine, cycloheptyl amine, cyclobutyl amine, cyclododecyl amine, 1-aminolindane, 2-aminoethanol, 2-methoxyethyl amine, 3-amino-1-propanol, 3-methoxy-1-propyl amine, 3-ethoxy-1-propyl amine, 3-((2-ethylhexyl)oxy)-1-propyl amine, 1-amino-2-propanol, 2-amino-1-butanol, 2-amino-2-methyl propanol, 2-amino-2-methyl-propane-1,3-diol and 2-amino-2-hydroxy-methyl propane-1,3-diol.

The addition of ammonia or primary amines to the unsaturated polyester resins results in the formation of structural units corresponding to the formula



wherein R' represents —NH_2 or —NHR .

The type and quantities of the reactants reacted with one another are selected so that amino-functional and optionally hydroxy-functional polyester resins have the characteristics mentioned above. When ammonia or amines which are gaseous at room temperature are used, excess quantities of the base are often added followed by the subsequent removal of the unreacted excess under vacuum and/or by the introduction of inert gas. When amines which are liquid at room temperature are used, the equivalent ratio of primary amino groups to structural units corresponding to the formula

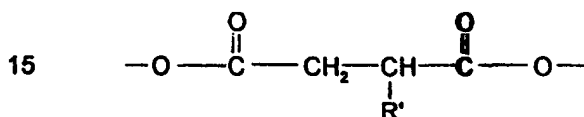


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can vary within wide limits, for example, from 0.05:1 to 1:1, preferably 0.1:1 to 1:1 and more preferably 0.1:1 to 0.6:1.

The reaction generally takes place at temperatures of 0 to 120°C, preferably 20 to 100°C. The reaction may be carried out in the presence or absence of suitable solvents depending upon the viscosity of the unsaturated polyester. Suitable solvents include toluene; xylene; higher alkylbenzenes; esters such as ethyl acetate, n-butyl acetate, methyl glycol acetate, ethyl glycol acetate and methoxybutyl acetate; ketones such as methyl ethyl ketone and methyl isobutyl ketone; and mixtures of these solvents.

As already mentioned, structural units corresponding to the formula:



wherein R' is defined as above, are formed in the reaction according to the invention. The reactivity of the amino group R' is greatly reduced by the electron-attracting effect when compared with corresponding, electron-unhindered amino groups.

One possibility of variation regarding the reactivity of the products according to the invention is to vary the ratio of incorporated hydroxyl groups to incorporated amino groups by suitable choice of the starting materials used in the process according to the invention and the quantities in which they are used.

Depending upon their molecular weight, the products obtained by the process according to the invention are generally low-viscosity to high-

viscosity, substantially colorless, clear resins which form clear solutions in the previously mentioned lacquer solvents.

The products obtained in accordance with the invention may be used in admixture with various quantities of other isocyanate-reactive compounds, preferably known polyester or polyacrylate polyols containing 0,5 to 10, preferably 1 to 5 % by weight of hydroxyl groups. This provides another possibility for controlling the reactivity of the component containing isocyanate-reactive groups. In general, the isocyanate-reactive component used in the application according to the invention contains up to 20 hydroxyl groups for every primary or secondary amino group. The ratio of (i) primary and/or secondary amino groups to (ii) hydroxyl groups in the binder component containing isocyanate-reactive groups is preferably 10:1 to 1:10. The percentage of products according to the invention in these mixtures is preferably 10 to 100% by weight. In a particularly preferred embodiment, the products according to the invention are used as sole isocyanate-reactive lacquer component.

Reactants for the "polyol component" in accordance with the invention are the known "lacquer polyisocyanates," i.e., the known urethane-modified, uretdione-modified or, in particular, biuret-modified or isocyanurate-modified diisocyanates. Examples of these diisocyanates include 1,6-diisocyanatohexane, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl cyclohexane (isophorone diisocyanate), 4,4-diisocyanatodicyclohexyl methane, 2,4- and 2,6-diisocyanatotoluene. "Lacquer polyisocyanates" containing aliphatically and/or cycloaliphatically bound isocyanate groups are particularly preferred.

Urethane-modified lacquer polyisocyanates are preferably reaction products of 2,4- and optionally 2,6-diisocyanatotoluene with less than equivalent quantities of trimethylol propane or mixtures thereof with

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simple diols such as the isomeric propane or butane diols. The production of these urethane-modified lacquer polyisocyanates in substantially monomer-free form is described, for example, in DE-PS 1,090,196.

- 5 Uretidione-modified lacquer polyisocyanates are preferably prepared from 1,6-diisocyanatohexane as described, for example, in EP-A-0,377,177.

- Biuret-modified lacquer polyisocyanates, which are preferred for the use according to the invention, are preferably those prepared from 10 1,6-diisocyanatohexane as described, for example, in EP-B1 0,003,505, DE-PS 1,101,394, US-PS 3,358,010 and US-PS 3,903,127.

- Isocyanurate-modified polyisocyanates, which are also preferred according to the invention, include in particular the isocyanate-functional trimers or mixed trimers of the previously disclosed diisocyanates.
- 15 Examples include the isocyanate group-containing polyisocyanates prepared from diisocyanatotoluene according to GB-PS 1,060,430, GB-PS 1,506,373 or GB-PS 1,485,564; the mixed trimers prepared from the diisocyanatotoluenes and 1,6-diisocyanatohexane in accordance with, for example, DE-PS 1,644,809 or DE-OS 3,144,672; and, in particular,
- 20 the aliphatic or aliphatic-cycloaliphatic trimers or mixed trimers prepared from 1,6-diisocyanatohexane and/or isophorone diisocyanate in accordance with, for example, US-PS 4,324,879, US-PS 4,288,586, DE-OS 3,100,262, DE-OS 3,100,263, DE-OS 3,033,860 or DE-OS 3,144,672.

- 25 The lacquer polyisocyanates employed in the use according to the invention preferably have an isocyanate content of 5 to 25% by weight and preferably have a residual content of the monomeric diisocyanates used for their production of less than 2% by weight. Mixtures of the

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previously mentioned lacquer polyisocyanates may also be used.

The two-component polyurethane coating compositions according to the invention are formulated to have an equivalent ratio of isocyanate groups to isocyanate-reactive groups of 5:1 to 1:2, preferably 1.5:1 to 1:1.2.

The two-component binders obtained by mixing the binder components have only a limited pot life of about 0.5 to 8 hours. They may be used for the production of clear or pigmented coating compositions which may contain known auxiliaries and additives. The auxiliaries and additives may be added either to the mixture or to the individual components before they are mixed.

Suitable auxiliaries and additives include the previously mentioned solvents; plasticizers such as tricresyl phosphate, phthalic acid diesters and chloroparaffins; pigments and fillers such as titanium dioxide, barium sulfate, chalk and carbon black; catalysts such as N,N-dimethyl benzylamine, N-methyl morpholine, zinc octoate, tin octoate and dibutyl tin dilaurate; flow control agents; thickeners; stabilizers such as substituted phenols; organofunctional silanes as coupling agents; and light stabilizers.

The light stabilizers include the sterically hindered amines described, for example, in DE-OS 2,417,353 (= US-PS 4,123,418 and US-PS 4,110,304) and DE-OS 2,456,864 (= US-PS 3,993,655 and US-PS 4,221,701). Particularly preferred compounds include bis-(1,2,2,6,6-pentamethyl-4-piperidyl)-sebacate, bis-(2,2,6,6-tetramethyl-4-piperidyl)-sebacate, n-butyl-(3,5-ditert.butyl-4-hydroxybenzyl)-malonic acid and bis-(1,2,2,6,6-pentamethyl-4-piperidyl)-ester.

The moisture adhering to the fillers and pigments may be removed by preliminary drying or by the use of water-absorbing materials such as

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molecular sieve zeolite.

The resulting coatings may be dried at room temperature. Drying does not require any increase in temperature to achieve optimum properties. However, elevated temperatures may be applied to
5 accelerate the drying reaction. Drying temperatures used for typical stoving conditions are possible, but less preferred. This is of considerable practical significance because, even at the relatively high temperatures which may occur, for example, in the event of malfunctions of lacquering plants, the coatings do not undergo thermal degradation.

10 Two-component polyurethane coating compositions containing the products according to the invention as their principal binder component are suitable for the production of coating compositions for any substrates such as metals, plastics, wood or glass.

Because they are equally suitable for plastics and metals, the
15 coating compositions according to the invention are also particularly suitable for coating substrates such as the exterior parts of automobiles produced from modern plastic/metal composites. The coating compositions according to the invention are particularly suitable for "on-line" coating of exterior auto parts because the coatings cure at low
20 temperatures so that the plastics are not exposed to high temperatures. Further, the resulting coatings show excellent weather resistance and elasticity so that decorative lacquer finishes remain unchanged for long periods and safely withstand impact stresses. The excellent chip resistance of automotive coatings produced in accordance with the
25 invention is also particularly emphasized in this regard. The coatings obtained with the two-component coating compositions according to the invention optimally satisfy basically conflicting requirements, i.e. excellent elasticity at low temperatures coupled with high resistance to solvents

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and tar stains, high gloss retention and resistance to yellowing on exposure to light of short wave length, for example, short-wave UV light.

The coating compositions according to the invention may be applied to the substrates to be coated by any known methods, for example, by spread coating, spray coating, roll coating or dip coating. The lacquers according to the invention are suitable for the production of base coats, intermediate coats and top coats.

In the following examples, all parts and percentages are by weight, unless otherwise indicated.

10

EXAMPLES

1. General procedure for the production of the unsaturated polyester precursors:

The monohydric and polyhydric alcohols and the unsaturated dicarboxylic acid(s)/anhydride(s) were weighed into a reactor equipped with a stirrer, heating system, automatic temperature control, column and receiver. The mixture was heated to 100-150°C while a stream of nitrogen was passed through the inhomogeneous mixture of starting materials. After the remaining dicarboxylic acids had been added, the mixture of starting materials was heated with stirring to 200°C over a period of 4 to 8 hours while nitrogen was passed through the mixture. The temperature measured at the head of the column was kept at a maximum of 105°C. The melt became homogeneous and clear. When the head temperature fell below 90°C, the column was removed and the mixture was condensed with an increased throughput of nitrogen to an acid value of < 3 mg KOH/g.

Colorless resins were obtained and were dissolved in methoxypropyl acetate, butyl acetate or mixtures thereof.

The composition and properties of the individual polyesters are

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given in Examples 1 and 2. The abbreviation "mol" applies to the molar ratio and not to the actual number of "moles," as can be seen from the quantities by weight in "g."

Example 1

| | | |
|----|--------------------------------|---------------------|
| 5 | Polyester A | Quantity weighed in |
| | 1.0 Mol hexane-1,6-diol | 526 g |
| | 1.0 Mol trimethylol propane | 596 g |
| | 1.5 Mol cyclohexane dimethanol | 962 g |
| 10 | 1.5 Mol neopentyl glycol | 696 g |
| | 2.2 Mol adipic acid | 1431 g |
| | 1.8 Mol maleic anhydride | 786 g |
| | Hydroxyl value: | 145 mg KOH/g |
| | Acid value: | 0.7 mg KOH/g |
| 15 | Molecular weight: | 1700 |

Example 2

| | | |
|----|------------------------------|---------------------|
| | Polyester B | Quantity weighed in |
| 20 | 4.00 Mol hexane-1,6-diol | 1949 g |
| | 1.00 Mol trimethylol propane | 553 g |
| | 0.52 Mol adipic acid | 314 g |
| | 0.52 Mol maleic anhydride | 211 g |
| | 2.48 Mol isophthalic acid | 1701 g |
| 25 | 0.48 Mol phthalic anhydride | 293 g |
| | Hydroxyl value: | 140 mg KOH/g |
| | Acid value: | 1.2 mg KOH/g |
| | Molecular weight: | 1800 |

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2. General procedure for the reaction of unsaturated polyesters with primary amines

Polyester precursors A and B from Examples 1 and 2 were optionally dissolved in a suitable solvent and introduced into a 2-liter four-necked flask equipped with a stirrer, thermometer, reflux condenser and dropping funnel and heated to 60°C. The corresponding primary amine was then added in one portion. The mixture was then stirred for 2 hours at 60°C, heated to 80°C and stirred until no more primary amino groups could be detected by titrimetry or until the solids content corresponded to the theoretical value of the amine addition. The product was then cooled and packed in containers.

3. General procedure for the reaction of unsaturated polyesters with ammonia

Polyester precursors A and B from Examples 1 and 2 were optionally dissolved in a suitable solvent and introduced into a 2 liter four-necked flask equipped with a stirrer, thermometer, reflux condenser and inlet pipe. Ammonia from a steel bottle was then passed through the flask for about 4 hours at room temperature. The reaction mixture heated up to about 30°C. The reaction mixture was then stirred for about 4 hours at room temperature, after which unreacted ammonia was driven out with nitrogen at 50°C. The product was then cooled and packed in containers.

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Table 1:

Aminopolyesters C to J according to the invention, quantities in g

| Example/aminopolyester | 3/C | 4/D | 5/E | 6/F | 7/G | 8/H | 9/I | 10/J | 11/K |
|---|------|------|------|------|------|------|------|------|------|
| Polyester A | 1200 | 1200 | 1200 | 1200 | 1200 | 1200 | 1200 | | 1200 |
| Polyester B | | | | | | | | 1200 | |
| Butyl acetate | 306 | 308 | 310 | 316 | 300 | 314 | 315 | 303 | 519 |
| Cyclohexylamine | 21.1 | 31.8 | 42.4 | 63.6 | | | | | |
| n-Butyl amine | | | | | 39.0 | | | | |
| 1-aminomethyl-3(4)-methyl-3-cyclohexane | | | | | | 53.5 | | 7.2 | |
| 3,3,3-trimethyl cyclohexyl amine | | | | | | | 60.5 | | |
| Ammonia | | | | | | | | | 10.7 |
| Solids content (%) | 79.8 | 79.5 | 79.3 | 79.1 | 79.6 | 79.7 | 80.2 | 79.4 | 70.0 |
| Viscosity at 23°C (mPas) | 3975 | 3850 | 3350 | 4080 | 3440 | 3800 | 5960 | 3610 | 7300 |
| NH + OH equivalent weight (g) | 466 | 449 | 439 | 421 | 423 | 444 | 446 | 495 | 447 |
| Amine nitrogen content (%) | 0.20 | 0.29 | 0.39 | 0.57 | 0.49 | 0.38 | 0.38 | 0.05 | 0.51 |

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5 Example 12 (Use)

This example describes the production of ready-to-use coating compositions prepared from the aminopolyesters of Examples 3 to 10 as well as from the polyesters of examples 1 and 2 (comparison), their application to substrates and the testing of the resulting coatings.

To evaluate the properties of the coating compositions, white compositions were produced by blending the polyesters of Examples 1 to 10 with various additives and white pigments and grinding on a Red Devil shaker.

A lacquer polyisocyanate was then added to provide an NCO/NH+OH equivalent ratio of about 1.3:1.

15 The "lacquer polyisocyanate" used was an isocyanurate group-containing polyisocyanate prepared from 1,6-diisocyanatohexane (Desmodur N 3390, a product of Bayer AG) which is present at 90% solids in a 1:1 ratio by volume of butyl acetate and Solvent Naphtha 100 solvent (NCO content of the solution: 19.4% by weight).

20 The following percentages of additives were used, based on solids (sum of the solid components of polyester and polyisocyanate):

Table 2

| Additives | % Solid on solid |
|---|---|
| 5 | Zinc octoate (10% in 1-methoxypropyl-2-acetate) 0.2 |
| 10 | Silicone oil as flow control agent (Baysilon lacquer additive OL 17, a product of Bayer AG; 10% in 1-methoxypropyl-2-acetate) 0.1 |
| 15 | Tinuvin 292 (a light stabilizer produced by Ciba-Geigy, Basel; 10% in xylene) 1.0 |
| 15 | Tinuvin 900 (a light stabilizer produced by Ciba-Geigy, Basel; 10% in xylene) 1.0 |
| 20 | Titanium dioxide (rutile type; Kronos 2160, a product of Kronos-Titan, Leverkusen) 60.0 |
| 25 | Antisedimenting agent (Bentone 38, a product of Kronos-Titan, Leverkusen; 10% suspension in a 17:1 blend of Solvesso 100 solvent and Antiterra U 17:1 additive) 1.0 |
| 25 | The solvent used was a mixture of ethyl acetate, 1-methoxypropyl-2-acetate and methyl ethyl ketone (1:1:1). The coating composition was diluted to a content of: |
| 30 | 33% binder 20% pigment approx. 1% additive approx. 46% solvent |
| The flow time (DIN 53211; 4 mm orifice) was approx. 18 seconds. The coating compositions were ready for spraying. | |

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The lacquers were applied to glass plates (wet film thickness approx. 100 μm), dried for 45 minutes at 80°C and stored for 14 days at room temperature. The dry film thickness was approx. 50 μm .

König hardness (DIN 53157), Gardner gloss at 60° (DIN 67530),

- 5 dissolvability by various solvents and resistance to tar were then determined. The resistance of the coatings to tar stains was a critical aspect of the invention.

- To test their flexibility at low temperatures, the coating compositions were sprayed onto primed 3 mm thick plastic plates of
- 10 Bayflex 91 (a product of Bayer AG, Leverkusen), dried for 45 minutes at 80°C and stored for 14 days at room temperature. The dry film thickness was approximately 35 μm . 2 cm wide and 15 cm long strips prepared therefrom were stored for approx. 30 minutes at various temperatures (room temperature: 5°C, 0°C, -5°C, ..., -40°C) in a low-temperature
- 15 chamber and then bent around a 1 inch mandrel at the particular temperature prevailing in the chamber. The temperature at which the coating broke was the criterion for low-temperature flexibility. The lacquers produced from the polyesters polyols of Examples 1 to 10 satisfied stringent elasticity requirements, even at low temperatures.
- 20 The test results of the coatings based on the aminopolyesters according to the invention of Examples 3 to 10 and Comparison Examples 1 and 2 are set out in Table 3.

Table 3:

Test results of coatings based on the aminopolyesters of Examples 3 to 10 according to the invention and Comparison Examples 1 and 2

| Coating based on the polyester of Example No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| König pendulum hardness (s) | 40 | 60 | 64 | 75 | 91 | 99 | 95 | 88 | 89 | 92 |
| Gardner gloss, 60° | 88 | 85 | 86 | 88 | 87 | 89 | 90 | 88 | 87 | 84 |
| Dissolvability ¹⁾ by xylene | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| MPA | 1 | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 1 | 1 |
| Exposure time: acetone | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 1 minute ethanol | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Tar resistance ¹⁾ after exposure for | | | | | | | | | | |
| 1 h | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 3 h | 0-1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Tar solution: 8 h | 1 | 1-2 | 0 | 0 | 0 | 0 | 0 | 0 | 0-1 | 1 |
| DBL 7399 ²⁾ 24 h | 2 | 2-3 | 0-1 | 0-1 | 0 | 0 | 0 | 0-1 | 1 | 1-2 |
| Low-temperature flexibility: coating breaks at (°C) | -35 | -25 | -35 | -35 | -30 | -25 | -30 | -30 | -30 | -20 |

¹⁾ 0 best value, 5 poorest value²⁾ Special tar solution of Daimler Benz AG for determining the tar resistance of auto lacquers, composition:

30.5% by weight of Carbowaxes EP KS (a product of Rütgerswerke AG)

62.0% by weight of Edenol D 81 (a product of Henkel KGaA)

2.7% by weight of Santicizer 160 (a product of Monsanto)

4.8% by weight of Palatrol O (a product of BASF)

5 Discussion of the results:

Highly flexible coatings were obtained with coatings based on the polyesters of Examples 1 to 10, the coatings of Examples 1, 3 and 4 providing the best results in regard to elasticity. The results of the tar resistance tests reflect in particular the excellent resistance to tar of the coatings of Examples 3 to 10 according to the invention in contrast to comparison coatings 1 and 2.

10 Example 13 (Use)

The aminopolyester (K) of Example 11 was used to formulate clear coatings with the lacquer polyisocyanate of Example 12 and applied to glass plates (dry film thickness approx. 60 μm). The crosslinking ratio and the solids content are set out in Table 4. Solvent resistance was tested by the cotton wool pad method under the drying conditions shown in Table 4. Hardness was determined by the pencil method.

Table 4:

Clear coating compositions based on the aminopolyester of Example 11
according to the invention

Results of the solvent resistance and pencil hardness tests

| | | |
|----|---|--------------------|
| 5 | Example | 13 |
| | Aminopolyester of Ex. | 11 |
| | NCO/NH+OH ratio | 1.2 |
| | Solvent | BuAc |
| 10 | Solids content (%) | 70 |
| | Drying | 40/80°C + 1d RT |
| | Dissolvability ¹⁾ by | |
| | xylene | 0 |
| 15 | Exposure time: MPA | 0 |
| | 1 minute acetone | 1 |
| | EtOH/H ₂ O 1:1 | 0 |
| | Pencil hardness | 3H |
| 20 | ¹⁾ 0 best value, 5 poorest value | |

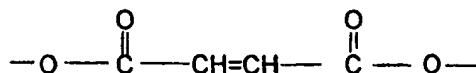
Although the invention has been described in detail in the
foregoing for the purpose of illustration, it is to be understood that such
detail is solely for that purpose and that variations can be made therein
by those skilled in the art without departing from the spirit and scope of

25 the invention except as it may be limited by the claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:-

1. process for the production of a polyester resin containing 0 to 10% by weight of hydroxyl groups and 0.01 to 9% by weight of nitrogen (expressed as N = 14) in the form of primary and/or secondary amino groups which comprises reacting in an addition reaction at 0 to 120°C
 - i) a polyester resin having a molecular weight (M_n) of 286 to 10,000 and containing an average per molecule of at least 2 structural units corresponding to the formula:

10



and optionally alcoholic hydroxyl groups with

- 15 ii) ammonia or a primary monoamine corresponding to the formula:

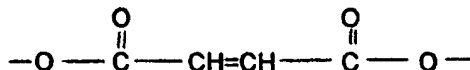


wherein

- 20 R represents an aliphatic, cycloaliphatic or araliphatic radical optionally containing ether oxygen atoms and/or hydroxyl groups.

2. The process of Claim 1 wherein component i) comprises an unsaturated polyester resin having a molecular weight of 488 to 8,000, a hydroxyl group content of 0 to 7% an average content of in all at least 3 structural units corresponding to the formula:

25



and is the reaction product of

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- 5 a) a polycarboxylic acid component consisting essentially of maleic acid, maleic anhydride and/or fumaric acid and up to 95 carboxyl equivalent-%, based on the total equivalents of component (a), of one or more polycarboxylic acids having a molecular weight of 118 to 1,000 and anhydrides of such acids with
- b) a polyol component having an average maximum hydroxyl functionality of 3 and consisting essentially of at least one polyhydric alcohol having a molecular weight of 62 to 400 and
- 10 c) optionally a monocarboxylic acid component in a quantity of up to 50 carboxyl equivalent-%, based on the total equivalents of components a) and c), and consisting essentially of least one monocarboxylic acid having a molecular weight of 60 to 400 and/or at least one anhydride of said monocarboxylic acid and/or
- 15 d) optionally a monohydric alcohol component in a quantity of up to 50 hydroxyl equivalent-%, based on the total equivalents of components b) and d), and consisting essentially of at least one monohydric alcohol having a molecular weight of 32 to 400,
- 20 while maintaining an equivalent ratio of carboxyl groups to hydroxyl groups of 1:1.5 to 1:1 and terminating the reaction when the acid value is below 10 mg KOH/g.

3. The process of Claim 1 wherein R represents an aliphatic or cycloaliphatic hydrocarbon radical having up to 15 carbon atoms optionally containing at least one alcoholic hydroxyl group.

25 4. The process of Claim 2 wherein R represents an aliphatic or cycloaliphatic hydrocarbon radical having up to 15 carbon atoms optionally containing at least one alcoholic hydroxyl group.

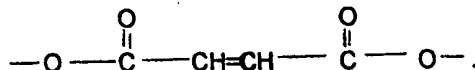
5. The process of Claim 1 characterized in that the reactants are present in amounts sufficient to provide 0.1 to 10 primary amino

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groups for each structural unit corresponding to the formula:



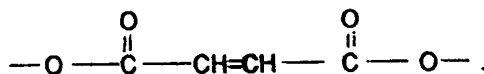
- 5 6. The process of Claim 2 characterized in that the reactants are present in amounts sufficient to provide 0.1 to 10 primary amino groups for each structural unit corresponding to the formula:



10

7. The process of Claim 3 characterized in that the reactants are present in amounts sufficient to provide 0.1 to 10 primary amino groups for each structural unit corresponding to the formula:

15



8. The process of Claim 4 characterized in that the reactants are present in amounts sufficient to provide 0.1 to 10 primary amino groups for each structural unit corresponding to the formula:

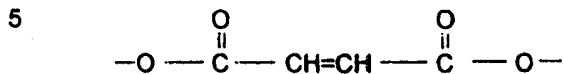
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- 25 9. A polyester resin containing 0 to 10% by weight of hydroxyl groups and 0.01 to 9% by weight of nitrogen (expressed as N = 14) in the form of primary and/or secondary amino groups which is prepared by a process which comprises reacting in an addition reaction at 0 to 120°C

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- i) a polyester resin having a molecular weight (M_n) of 286 to 10,000 and containing an average per molecule of at least 2 structural units corresponding to the formula:



and optionally alcoholic hydroxyl groups with

- ii) ammonia or a primary monoamine corresponding to the formula:

10

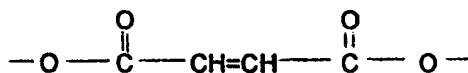


wherein

R represents an aliphatic, cycloaliphatic or araliphatic radical optionally containing ether oxygen atoms and/or hydroxyl groups.

- 15 10. The polyester resin of Claim 9 wherein component i) comprises an unsaturated polyester resin having a molecular weight of 488 to 8,000, a hydroxyl group content of 0 to 7% an average content of in all at least 3 structural units corresponding to the formula:

20



and is the reaction product of

- a) a polycarboxylic acid component consisting essentially of maleic acid, maleic anhydride and/or fumaric acid and up to 95 carboxyl equivalent-%, based on the total equivalents of component (a), of one or more polycarboxylic acids having a molecular weight of 118 to 1,000 and anhydrides of such acids with
- 25

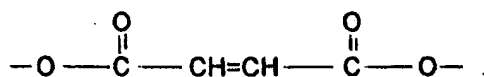
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- b) a polyol component having an average maximum hydroxyl functionality of 3 and consisting essentially of at least one polyhydric alcohol having a molecular weight of 62 to 400 and
- c) optionally a monocarboxylic acid component in a quantity of up to 50 carboxyl equivalent-%, based on the total equivalents of components a) and c), and consisting essentially of at least one monocarboxylic acid having a molecular weight of 60 to 400 and/or at least one anhydride of said monocarboxylic acid and/or
- d) optionally a monohydric alcohol component in a quantity of up to 50 hydroxyl equivalent-%, based on the total equivalents of components b) and d), and consisting essentially of at least one monohydric alcohol having a molecular weight of 32 to 400,
- while maintaining an equivalent ratio of carboxyl groups to hydroxyl groups of 1:1.5 to 1:1 and terminating the reaction when the acid value is below 10 mg KOH/g.

11. The polyester resin of Claim 9 wherein R represents an aliphatic or cycloaliphatic hydrocarbon radical having up to 15 carbon atoms optionally containing at least one alcoholic hydroxyl group.

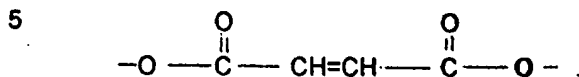
12. The polyester resin of Claim 10 wherein R represents an aliphatic or cycloaliphatic hydrocarbon radical having up to 15 carbon atoms optionally containing at least one alcoholic hydroxyl group.

13. The polyester resin of Claim 9 characterized in that the reactants are present in amounts sufficient to provide 0.1 to 10 primary amino groups for each structural unit corresponding to the formula:

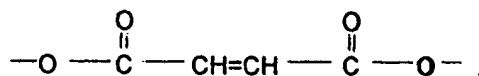


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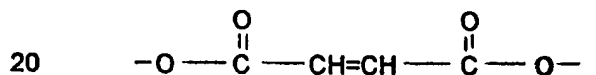
14. The polyester resin of Claim 10 characterized in that the reactants are present in amounts sufficient to provide 0.1 to 10 primary amino groups for each structural unit corresponding to the formula:



15. The polyester resin of Claim 11 characterized in that the reactants are present in amounts sufficient to provide 0.1 to 10 primary amino groups for each structural unit corresponding to the formula:



15 16. The polyester resin of Claim 12 characterized in that the reactants are present in amounts sufficient to provide 0.1 to 10 primary amino groups for each structural unit corresponding to the formula:



25 17. A two-component polyurethane coating composition wherein the binder comprises a polyisocyanate, the polyester resin of Claim 9 and optionally other one or more other compounds containing isocyanate-reactive groups.